

PHOTOCATALYTIC DETOXIFICATION OF CHLOROBENZENE IN AQUEOUS SOLUTIONS

ABSTRACT:

This study investigated the effectiveness of commercial catalyst (titanium dioxide and zinc oxide) and locally prepared periwinkle shell ash (PSA) and snail shell ash (SSA) in photo-detoxification (degradation) of chlorobenzene. The study was carried out in a slurry batch system in sunlight and in the dark. The optimum substrate concentration, optimum catalyst dosage, and optimum pH were investigated. The PSA and SSA were characterized using Fourier Transform Infra-Red (FTIR) analysis. The results show that for the degradation of chlorobenzene, the sunlight reaction was much better than the dark reaction irrespective of the catalysts used. The order was titanium dioxide > zinc oxide > PSA > SSA. The percentage degradation for the sunlight reaction was 46.85% for titanium dioxide, 41.30% for zinc oxide, 26.02% for PSA and 16.02% for SSA respectively. The optimum substrate concentration, catalyst dose and pH were 100mg/L, 2g/L and 7g/L respectively.

Keywords: Chlorobenzene, Photocatalysis, Degradation, Periwinkle shell, Snail shell, Titanium oxide, Zinc oxide

1 INTRODUCTION

Chlorobenzenes, which are chlorinated derivatives of benzene, are stable, colorless, pleasant smelling organic compounds. These compounds do not occur widely in nature, but manufactured for use as solvents and also used in the production of other chemicals (Agency for Toxic Substances, 1990).

Chlorobenzenes may polymerize to biphenyls, chloronaphthalenes, or more complex products. The ability of chlorobenzenes to undergo wide varieties of chemical reactions makes chlorinated benzenes useful as reactants in numerous commercial processes to produce varied products. All chlorinated derivatives of chlorobenzenes are currently principally used as chemical intermediates in the production of chemicals such as nitrochlorobenzenes and diphenyl oxide. These chemicals are subsequently used in the production of herbicides, dyestuffs, and rubber chemicals. Additionally, monochlorobenzene is used as a solvent in degreasing processes (for example, in metal cleaning operations), paints, adhesives, waxes and polishes (Kometani et al., 2008). Other applications include use as a fiber-swelling agent and dye carrier in textile processing; as tar and grease remover in cleaning and degreasing operations; as a solvent in surface coating and surface coating removers; and as a heat-transfer medium. (EPA, 1995). Both industrial and human activities have resulted in chlorobenzene contamination of air, soil, surface water and underground water. As a result, humans can be exposed to chlorobenzene by breathing contaminated air, by drinking water or eating food contaminated with chlorobenzene, or by getting chlorobenzene contaminated soil on the skin. These exposures are most likely to occur in the workplace or near chemical waste sites.

The removal of organic pollutants from water and wastewater has received a great deal of attention not only because of their contamination of water bodies but also the resulting deleterious effects they have on humans, flora and fauna.

Heterogeneous photo-catalysis is one of the most used technologies for treatment of polluted water. Chlorobenzene is listed as a priority pollutant and has a permissible limit of 3 mg/L (Dhananjay, 2004). The ability of photoactivated TiO_2 to oxidize organic molecules is based on hydroxyl radical, which is the primary oxidant in the photocatalytic system. (Huang et al., 2009). The aims and objectives of this study include: the degradation of chlorobenzene using titanium dioxide, zinc oxide, periwinkle shell and snail shell ashes with natural ultraviolet (UV) radiation from the sun and the evaluation of the potentials of periwinkle shell and snail shell ashes as locally sourced photo-catalysts

2 MATERIALS AND METHODS

2.1 Preparation of Adsorbent (Periwinkle shell and Snail Shell)

Snail and periwinkle shell were obtained from Warri in Delta State of Nigeria. They were washed and dried in an oven at 110°C to constant mass, followed by crushing, then activated at 600°C in a muffle furnace. It was sieved after grinding to obtain fine particle size ($< 350\mu\text{m}$). The periwinkle shell ashes were tagged PSA while the snail shell ashes were tagged SSA. The prepared ashes were characterized by analyzing for the elemental compositions (especially the transition elements) using Fourier Transform Infra-red (FTIR) analysis.

Titanium Oxide (TiO_2) was procured from BDH Chemical Ltd, Pools, England. It is Anatase with minimum assay 99.0%, density of 4.23 and melting point of 1855°C .

Zinc Oxide (ZnO) was procured from Fischer Scientific Company, chemical manufacturing division, Fair Lawn, New Jersey, U.S.A.

All the solutions were prepared in distilled water-ethanol mixture, with the pH adjusted using 0.5M HCl and 0.1M NaOH solutions.

2.2 Preparation of Standard Solutions

Stock solution (500 mg/L) of chlorobenzene with 1:1 ratio of chlorobenzene-ethanol solution was prepared with distilled water. Varying concentration of chlorobenzene solution was prepared from the stock using varied dilution ratio.

2.3 Apparatus and Equipment

UV/VIS spectrophotometer Model T70 with printer, was used for determining concentration of chlorobenzene at a wavelength (λ) = 221.5nm. Fourier Transformed Infra-red (FTIR) spectrometer Model 8300 was used to determine the functional groups in the adsorbents. Air bath Shaker Model THZ-82, and Orbital shaker Model OS-752 OPTIMA, were used in shaking samples for dark and sunlight adsorption respectively.

2.4 Chlorobenzene Adsorption Studies

Dark adsorption and exposure of setup to sunlight adsorption (photocatalysis) were studied. In the case of dark-adsorption studies, 100 cm^3 aliquot with an initial concentration of 100 mg/L were mixed with 2g each of the four catalysts (TiO_2 , ZnO , PSA and SSA) and shaken for 1hr to allow equilibrium to be reached. The effects of catalyst dosage, initial substrate concentration, pH variation as well as time variation were then noted.

3 RESULTS AND DISCUSSION

3.1 The Results for the Elemental Analysis of Periwinkle Shell and Snail Shell Ashes

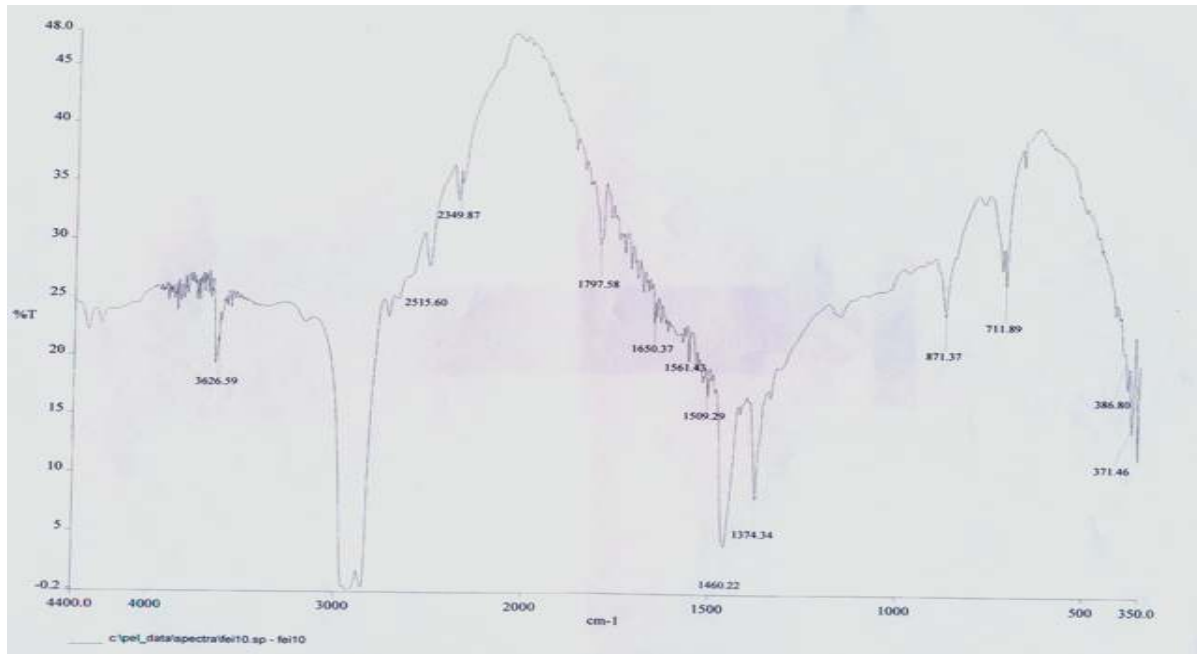


Figure 1: FTIR for Periwinkle shell ashes

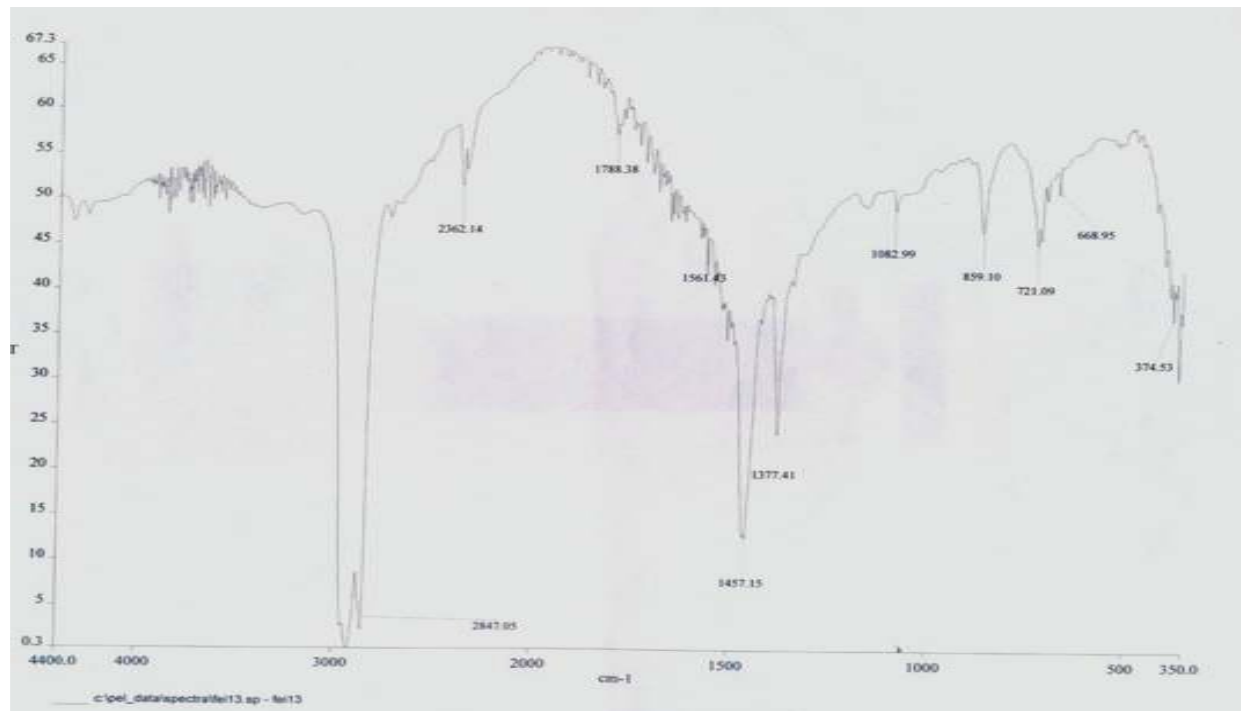


Figure 2: FTIR for Snail shell ashes

Figures 1 and 2 show the FTIR (Fourier Transform Infrared) for PSA and SSA respectively, the FTIR peaks shows the various functional groups present in the respective shell ashes. The corresponding functional groups for PSA were; alcohol (O-H), carboxylic acids (-COOH), anhydride (C=O), Amides (-CONH₂), aromatic ring (), nitro groups (N=O), alkene (=C-H), alkyl halide (-C-Cl), nitro- amines (N-H Bond). Functional groups of the SSA were; Aldehydes (R-CHO), Carbonyl (C=O), Aromatic ring () Nitro group (N=O), Amines-Secondary (N-H Bond), Alcohol (C-OH), Alkene (=C-H), Alky halide (-C-Cl). Sujoy et al., (2008) reported that the presence of these functional groups enhances adsorption of the substrate to the adsorbent and that carboxyl group as important moiety involved in the binding process. From these we can see how the interaction of the present bond in the functional group aid adsorption of the substrate to the adsorbent surface.

The result of the various metals observed in PSA and SSA, whose oxides have some photocatalytic properties that can enhance photo-degradation of organic pollutant is shown in Table 1.

Table 1: The results for the elemental analysis of PSA and SSA

S/N	PARAMETER	PSA	SSA
1.	Iron (Fe)	19.2	20.5
2.	Chromium (Cn)	6.3	7
3.	Vanadium (V)	1.5	2.5
4.	Nickel (Ni)	9	10.5
5.	Selenium (Sc)	0.125	0.075
6.	Lead (Pb)	0.075	0.125
7.	Aluminium (Al)	12.3	11.0
8.	Zinc (Zn)	16.5	16.5
9.	Tin (Sn)	8.0	7.0
10.	Cadium (Cd)	0.05	0.08
11.	Copper (Cu)	2.4	1.8
12.	Asenium (As)	ND	ND

ND = Not detected

3.2 Investigation of the Photocatalytic property of snail and periwinkle shell

Figure 3 shows the percentage of chlorobenzene (CB) degraded in dark adsorption and adsorption under sunlight. It was observed that 29.37% of CB was degraded in the dark compare to 46.85% in sunlight using titanium dioxide. The zinc oxide catalyst gave 24.92% for dark and 41.30% for sunlight. In addition, PSA gave 8.15% for dark and 26.02% for sunlight and lastly, the dark and sunlight degradation using SSA catalyst were 6.56% and 16.25% respectively. Generally, the percentage degradation for sunlight adsorption was far more promising than dark adsorption.

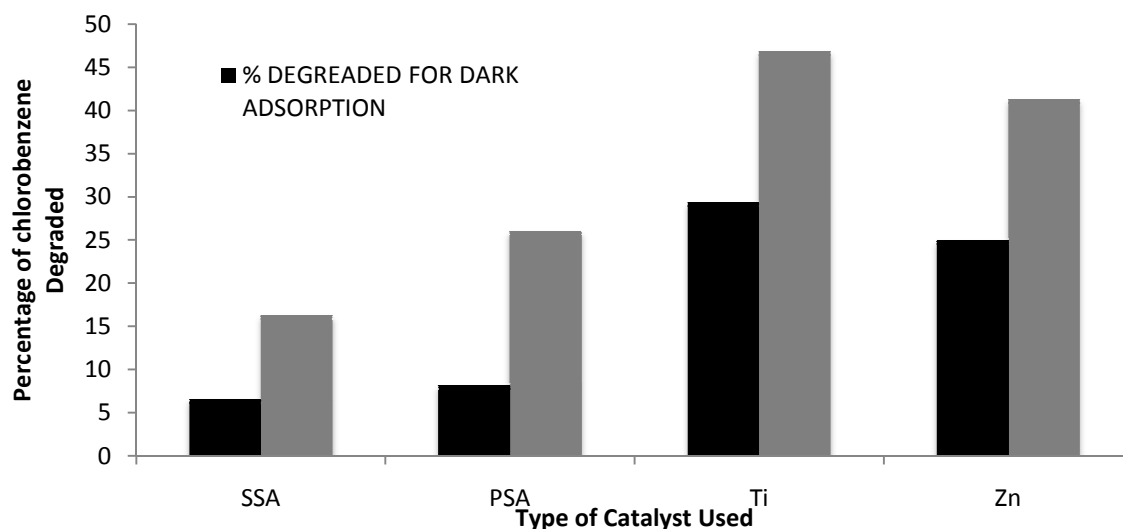


Figure 3: Percentage chlorobenzene degraded in dark and under sunlight UV

3.3 Effect of Catalyst Dosage

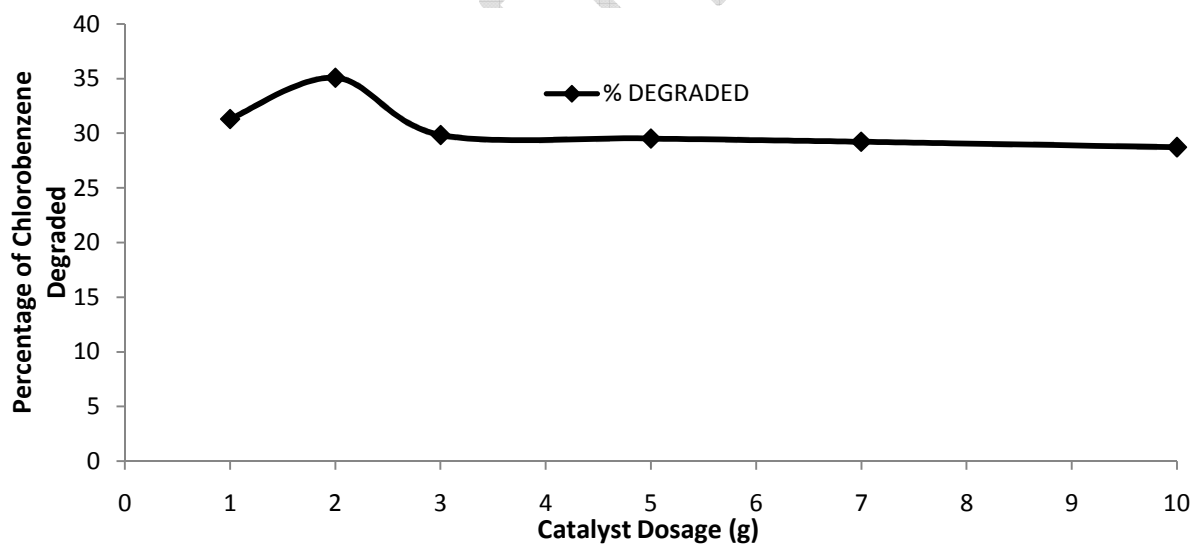


Figure 4: Percentage of chlorobenzene degraded with varying amount of PSA

From Figure 4, it was observed that the degradation of CB increased from 31.31% to 35.08% as the catalyst loading increased from 1g to 2g. With catalyst loading of 3g the CB degradation fell to 29.84%, which remained almost constant up to a catalyst loading of 10g. This can be explained by the fact that when the optimum amount of catalyst for a particular degradation is exceeded, no appreciable increment in the amount of chlorobenzene degraded will be noticed as a result of clogging. Dhananjay et.

al, (2004) reported that with a catalyst loading of 0.2% (w/v) of solution no chlorobenzene was detected after 15min of study under UV, whereas a relatively small amount of chlorobenzene was detected after dark adsorption. With 10mg of catalyst loading for 400cm³ of water containing 500mg/L of initial chlorobenzene, negligible concentration was observed after 15 min in the case of UV study.

3.4 Effect of Initial Substrate Concentration

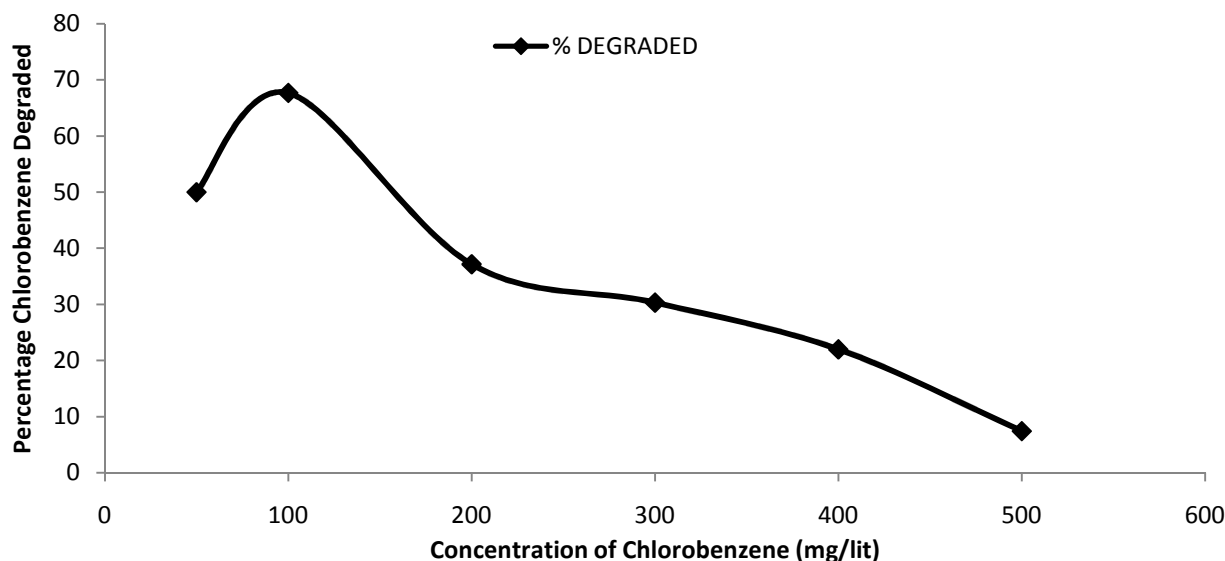


Figure 5: Percentage degraded with varying concentration of chlorobenzene

Figure 5 shows the variation of percentage degradation of CB with its initial substrate. For concentration of 50mg/L of CB, 50% CB was degraded while 67.67% CB was degraded at a concentration of 100mg/L,. As the concentration of the CB increases, the degradation drastically reduces to 7.47% at a CB concentration of 500mg/L. This observation can be explained from the fact that as the concentration increases, the amount of substrate available for the same conditions of degradation increases. Therefore, the amount degraded relative to that initially present becomes relatively small, this accounts for the percentage degradation reduction. Frank et. al. (1992) reported that at lower concentration of substrate, the degradation is proportional to the concentration. The reaction is now limited by diffusion to the semiconductor surface which may result in a pseudo first order kinetics.

3.5 Effects of varying pH

As can be seen from Figure 6, a better degradation of chlorobenzene is obtained at a pH of 6.7 to 7 (neutral range). This agrees with the works of Dhananjay et al. (2004). They reported that maximum adsorption is attained at a pH of 7 and that degradation is maximised at this pH. In his work, Dianlu (2004) noted that although cases have been presented where pH greatly changed the photo-catalytic rates, in a vast majority of cases, the rate of photo-catalytic reaction is found to be only weakly dependent on pH of solution. Hamdi et al., (2004) on the other hand noted that the optimal pH for adsorption was located between 3 and 5. Adsorption at near-acid pH could be attributed to the clay part of the geo-material sample. This could probably be due to the surface complexation phenomenon, which is facilitated by dissociation of the acidic functional groups present in the geo-material (Hamdi et. al, 2004)

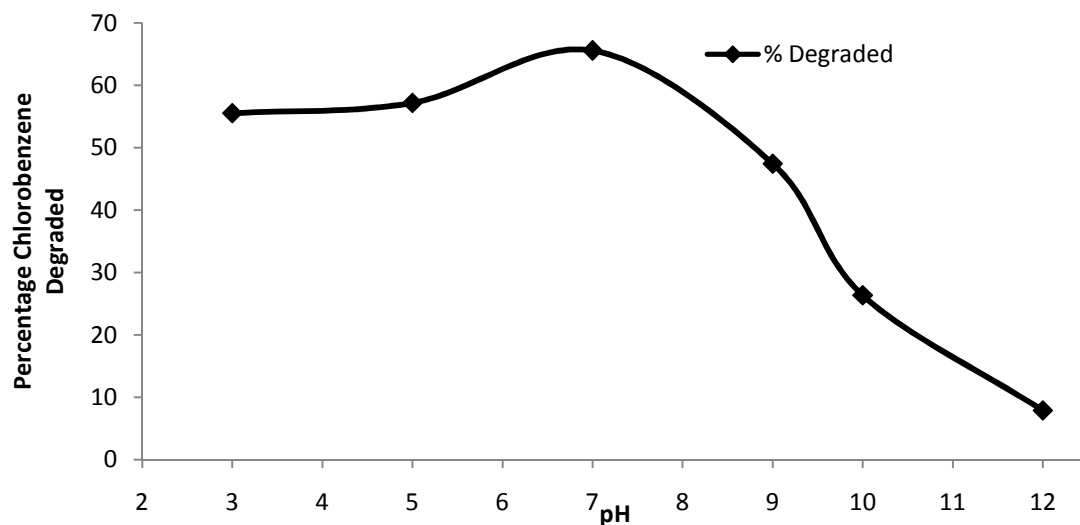


Figure 6: Effect of varying pH on the degradation of Chlorobenzene

3.6 Effect of Time Variation

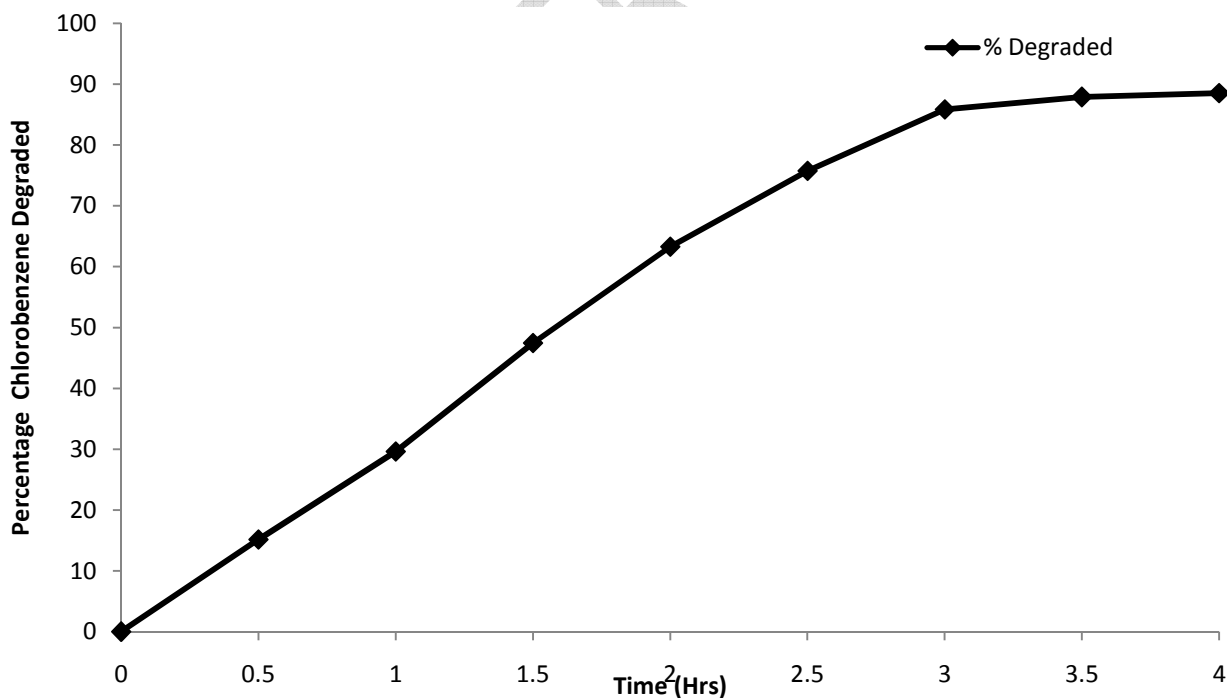


Figure 7: Percentage of chlorobenzene degraded with time

Figure 7 shows percentage degradation of CB with time. It was observed that at the early stage of the degradation, (i.e. the first 30mins) the percentage degradation of CB was 15.15%. However, this increased to 29.63% and 85.86% after 1 hr and 3 hrs respectively. Furthermore, 88.55% of chlorobenzene

was degraded at the end of 4 hrs. This shows that at the end of the first 3 hrs, the degradation process began to attain equilibrium, which at the end of the 4 hrs had only a difference of 2.69% as compared to the first 30 minutes.

4 CONCLUSION

The following conclusions can be drawn from this study:

- PSA and SSA have the potential for photocatalytic degradation of chlorobenzene in aqueous solution.
- Solar photocatalytic degradation has been proved to be more effective than adsorption alone for the degradation of chlorobenzene using titanium dioxide, zinc Oxide, SSA and PSA.
- The optimum conditions for degrading chlorobenzene are at a catalyst dose of 2mg/lit, initial substrate concentration of 100mg/lit, pH of 7 and 2ml of H₂O₂.
- Finally, over 89% degradation of chlorobenzene can be obtained upon the use of PSA and SSA as photocatalyst.

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